Doping and Field-Induced Insulator-Metal Transitions in Half-Doped Manganites

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(Dated: February 2, 2008)

We argue that many properties of the half-doped manganites may be understood in terms of a new two-(e_g electron)-fluid description, which is energetically favorable at intermediate Jahn-Teller (JT) coupling. This emerges from a competition between canting of the core spins of Mn promoting mobile carriers and polaronic trapping of carriers by JT defects, in the presence of CE, orbital and charge order. We show that this explains several features of the doping and magnetic field induced insulator-metal transitions, as the particle-hole asymmetry and the smallness of the transition fields.

"Half-doped" manganites such as $Re_{1-x}A_xMnO_3$ with $x = 1/2$ where Re is a 3+ rare-earth ion and A a 2+ alkaline earth ion have been the object of extensive studies for many years [1]. The lowest temperature phase seems to be either the CE phase, consisting of ferromagnetic *zig-zag chains* with relative antiferromagnetic (AF) order (as in $La_{1/2}Ca_{1/2}MnO_3$, where it was first proposed [2, 3], and in $Nd_{1/2}Sr_{1/2}MnO_3$ [4] or $Nd_{1/2}Ca_{1/2}MnO_3$ [5]) or an A-type phase, i.e, ferromagnetic *planes* with relative AF alignment (as in $Pr_{1/2}Sr_{1/2}MnO_3$ [4]). The competition between the CE and A phases appears even in a simple one-orbital model [6] because of the interplay of ferromagnetic double-exchange and AF superexchange between the core t_{2g} spins of Mn (see also Fig. 1). The presence of charge and orbital order as proposed by Goodenough [3] is more difficult to establish. X-ray diffraction experiments do suggest the presence of large Jahn-Teller (JT) distortions [4, 7] with two inequivalent Mn sites. In the CE phase, the alternating $(3x^2 - r^2)/(3y^2 - r^2)$ orbital order (consistent with the observed distortions) was shown to optimize the anisotropic hopping energy of the e_g electrons in a more realistic two e_g orbital model [8]. The origin of charge-order was attributed to on-site [8] or intersite Coulomb interactions [9, 10], though the latter tends to favor a Wigner crystal [9] rather than the charge stacked order found experimentally [1]. The role of the JT coupling has been investigated using imposed JT distortions [11] as well as by extensive classical Monte-Carlo simulations that lead to the observed charge stacked ordering [12].

However, several fundamental issues remain to be understood. One of them is the striking asymmetry with respect to the addition of electrons or holes. Experimentally, added electrons typically favor ferromagnetic metallic phases while added holes favor insulating phases [1]. In contrast, band structure arguments [8], and treatments including JT distortions adiabatically and classically [12] lead to metallic phases on both sides. Another puzzling feature, first seen in $(Nd,Sm)_{1/2}Sr_{1/2}MnO_3$ [13] and later seen to be ubiquitous [1], is that magnetic-fields $\sim 10-40$ Tesla, which are extremely small compared with Néel or charge ordering temperatures ~ 200 K, induce an insulator-metal transition. This can be viewed as another manifestation of the colossal magneto-resistance (CMR) in doped manganites [1]. An explanation is that this arises from the proximity of the CE phase to a ferromagnetic phase [6, 10, 14]; but it is difficult to understand why the parameters in so many systems should all be so finely tuned as to be near the phase boundary.

Recently, starting from a large JT coupling picture, a two-fluid e_g electron model, one polaronic and localized, and the other band-like and mobile, was proposed and shown to explain, in particular, the CMR in the orbital liquid regime [15]. In this letter, we show how the two types of electrons can emerge from a realistic microscopic model, even at intermediate JT couplings, in the half-doped case where orbital and charge order have to be explicitly included. Basically, they arise from a competition between canting of the Mn core spins promoting mobile carriers, and the JT coupling promoting polaronic, localized carriers. We show that our picture leads to natural explanations for the particle-hole asymmetry around half-doping as well as the magnetic-field-induced insulator-metal transition at half-doping mentioned above. Interestingly, a similar two-carrier-type hypothesis was proposed *based on phenomenological grounds* in Ref. 16 to understand resistivity data in $La_{1-x}Ca_xMnO_3$ ($x \sim 1/2$); for which our theory provides a microscopic basis. JT distortions were recently tracked as function of field in $La_{1/2}Ca_{1/2}MnO_3$ and shown to play a crucial role near the field-induced transition [17, 18]; our picture is completely consistent with this. We believe that the ideas presented here may be relevant to other classes of systems such as CsC_{60}, in which a similar two-electron phase has been proposed [19].

Our theory is based on the following microscopic two-orbital Hamiltonian for the manganites:

$$\mathcal{H}[\{\mathbf{S}_{ia}, Q_{ia}, \Theta_{ia}\}] = -\sum_{ij\alpha\beta ab} \tilde{t}^{\alpha\beta}_{abij}(\mathbf{S}_{ia}, \mathbf{S}_{jb}) c^\dagger_{ia\alpha} c_{jb\beta}$$

$$+ \sum_{<ia,jb>} J_{AF} \mathbf{S}_{ia} \cdot \mathbf{S}_{jb} - g\mu_B \sum_{ia} \mathbf{H} \cdot \mathbf{S}_{ia}$$
$$+ \frac{1}{2} K \sum_{ia} Q_{ia}^2 - g \sum_{ia\alpha\beta} Q_{ia} c_{ia\alpha}^\dagger \tau_{\alpha\beta}(\Theta_{ia}) c_{ia\beta}. \quad (1)$$

Here $c_{ia\alpha}^\dagger$ creates an electron in the e_g orbital α ($= x^2-y^2,\ 3z^2-r^2$) in the unit cell i and a sublattice site labelled by a. (We use a 8-sublattice decomposition to accommodate the CE phase.) There are N sites and cN electrons with $c \equiv (1-x)$ close to 1/2. Due to a large Hund's coupling J_H the electron spin is assumed to be locked parallel to the $S = 3/2$ t_{2g} core spins of Mn, modelled as *classical vectors* $\mathbf{S}_{ia}$. The hopping parameters (with $4t/3$ being the hopping between $(3z^2-r^2)$ orbitals in the z-direction) include the standard Anderson-Hasegawa dependence on $\mathbf{S}_{ia}, \mathbf{S}_{jb}$ that takes care of this large J_H projection [12]. The core spins are directly coupled by an AF superexchange, $J_{AF}S^2 \sim 0.1t$ [12]. $\mathbf{H}$ is the external magnetic field. The last two terms include the vibrational energy of JT phonons (where K is the lattice stiffness of a simplified non-cooperative model) and their coupling to the e_g electrons. Q_{ia} and Θ_{ia} represent the amplitude and the angle of the two (Q_2, Q_3) JT modes, and the τ matrix the symmetry of their coupling [12]. On-site Coulomb interactions can be ignored in a first approximation when large JT distortions are present (as the JT coupling suppresses double occupancy) and for large J_H.

We have determined the ground state of (1) exactly numerically, *but in the subspace of spin and distortion variables restricted to be periodic with a unit cell of at most 8 sites*. This accommodates the CE state as well as several other competing commensurate states. Compared to earlier numerical approaches [12] that were limited to small clusters, our calculations are practically in the thermodynamic limit. We confirm the phase diagram that was previously obtained [12, 14] and obtain detailed predictions on the strength of the JT-distortions Q, etc. [20]. The phase diagram is given in Fig. 1 and the phases are described in the figure caption. The strong-coupling phases, all insulating and charge ordered, can be understood by starting from localized Wannier orbitals centered on alternate JT distorted sites which are fully occupied. By *virtual double exchange* involving neighboring empty sites with aligned core spins [15], the electrons gain energy in a way that depends upon the orientation of the JT distortion or occupied orbital [20]. A comparison of the energies of the various phases leads to the sequence of first-order transitions at couplings given by $J_{AF}S^2 = 4tK/(9g^2)$ and $J_{AF}S^2 = 8tK/(9g^2)$ (dotted dashed lines in Fig. 1).

Phases that are inhomogeneous or incommensurate [21] can not be captured by the above analysis because of the limited size of the maximal unit-cell. We tackle this problem, albeit to a limited extent, by studying the

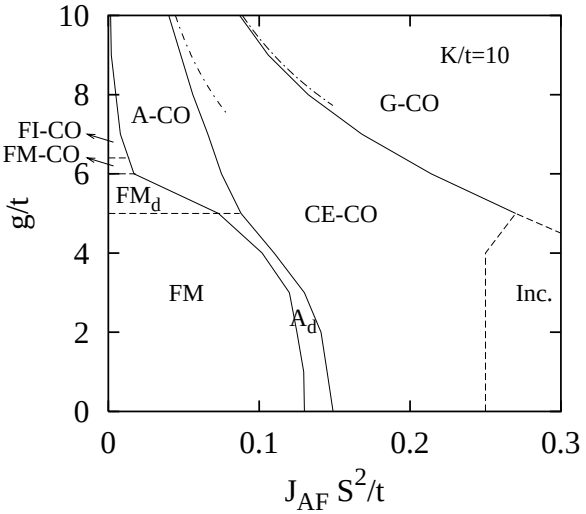

FIG. 1: Phase diagram of the 3D two-orbital model ($T = 0$, $x = 0.5$, $K/t = 10$). FM (resp. FM$_d$): ferromagnetic metallic phase with no distortions (resp. small uniform distortions). FI-CO (resp. FM-CO): charge-ordered ferromagnetic insulating (resp. metallic) phase with distortions that favor occupancy of the x^2-y^2 orbitals. A$_d$: ferromagnetic planes AF aligned with uniform distortions. A-CO: A with charge order. CE-CO: Ferromagnetic zig-zag chains AF ordered, orbital ordered ($3x^2-r^2/3y^2-r^2$ on the bridge sites), and charge-ordered ($g/t > 0$). G-CO: Néel AF phase with charge-order. Inc.: incommensurate state that interpolates between CE and G. Dotted dashed lines come from analytical expressions derived in the strong-coupling limit. Solid (dashed) lines show first-order (second-order) phase transitions.

instabilities of the homogeneous insulating phases discussed above with respect to particle or hole excitations *accompanied by single site defects in their JT distortion pattern*. For this, we find the electronic eigenvalues of (1) in the *presence of such defects* numerically (with N up to 1728), and calculate the energy cost or gain from filling the energy levels with cN electrons.

To start with, consider the FI-CO phase at strong-coupling, with the electrons localized at the JT distorted sites with distortion Q. If we now promote a particle across the charge gap, it is energetically favorable for the JT distortion at the hole site (from which the electron is removed) to relax to $Q - Q_d$. The loss in electronic energy due to the scattering of the other electrons from the defect is overcompensated by the gain in elastic energy. The hole gets polaronically trapped, while the electron is mobile. Such mixed excitations thus have energies lower than the energies of particle-hole excitations due to band structure alone. For the FI-CO phase, this is demonstrated in Fig. 2 where, in addition to the minimum at $Q_d = 0$ (corresponding to the homogeneous phase), there is another minimum at $Q_d \sim Q$, corresponding to the removal of the JT distortion at one site. Furthermore, this minimum softens when g/t is reduced below $g/t \sim 6.8$ (Fig. 2), although the other homogeneous phases of Fig.

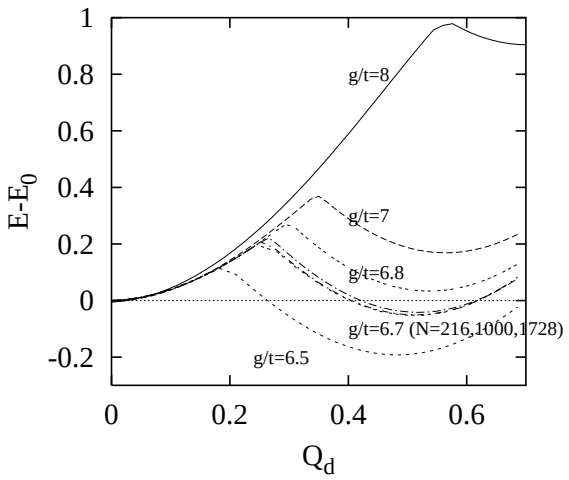

FIG. 2: Energy change when a single JT defect is introduced in the FI-CO phase. $Q - Q_d$ is the JT distortion on a defect site; all the other occupied sites having the same distortion Q. The softening of the excitation with $Q_d \sim Q$ at $g/t \sim 6.8$ signals a phase transition with proliferation of defects. Finite-size effects are small and shown for $g/t = 6.7$.

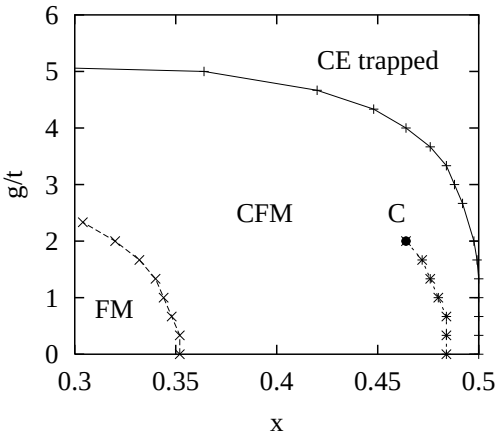

FIG. 3: Phase diagram, g/t vs. doping, x ($J_{AF}S^2/t = 0.15$). CFM: canted CE state with distortions and charge-order (metallic). CE trapped: CE phase with extra carriers trapped in JT distortions (insulating). FM: ferromagnetic metallic phase with no distortions. The upper curve is valid for x close enough to 0.5. C is a critical point ending a first-order line between two canted states (with different canting angles).

1 are at higher energy at this g/t. The instability approach therefore suggests that there might be another phase where such defects are energetically favorable and proliferate. With a small number of *the above type of defects*, a small fraction of electrons are converted from localized to mobile states leading to a metal with a small concentration of mobile electrons. This is reminiscent of the two-fluid picture [15], but now extended to accommodate orbital and charge order [20].

We next address similar instability issues in the context of the CE phase. First consider what happens when the CE phase is doped with carriers. As discussed above, experimentally there is a strong asymmetry between hole and electron doping. According to de Gennes's original argument [22], canted phases are expected for small doping (irrespective of their sign). It is known that the energy of the fully ferromagnetic state crosses that of the CE state when extra electrons are added [8], but intermediate canted phases have not been considered. They would naively lead to second-order transitions rather than first-order. We have studied such canted phases and obtained the optimal canting angle as function of x close to 1/2. Similarly to the discussion above in the context of the FI-CO phase, these homogeneous phases are in competition with inhomogeneous phases where the added carriers are self-trapped by JT distortions. In fact, we find that it is favorable to trap the added *carriers* at small $\delta c \equiv 1/2 - x$. This leads to an insulating un-canted CE phase (noted CE trapped in Fig. 3). On the *electron*-doped side ($x < 1/2$, Fig. 3), increasing δc leads eventually to a canted metallic phase (CFM) via a first-order transition. This is because the JT energy gain due to trapping is linear in δc, $\delta E_{tr} = -\tilde{E}^{e,h}_{JT}|\delta c|$ (with $\tilde{E}^{e,h}_{JT}$ obtained by solving, for all g/t, the one-defect problem mentioned above with one added carrier) [20], whereas the energy gain from canting is quadratic, $\delta E_{ca} \sim -(\delta c)^2$ [22]. The latter loses for small δc but wins for larger δc. On the *hole* side, however, we find that canted phases are never energetically favorable. The asymmetry arises because of the nature of the CE ordering. Canting leads to a 2-d dispersion, with a large density of states at the bottom of the conduction band (for electron doping), whereas it gives a 3-d dispersion, with a vanishing DOS at the top of the valence band (for hole doping). Therefore, canting angles can indeed get large when electrons are added and compete effectively against electron trapping. But when holes are added, canting angles are much smaller and the holes get trapped by JT distortions for $g/t > 4$. Hence the system remains insulating. Thus, our approach leads to an explanation for the asymmetry between particle and hole doping seen experimentally. It also helps us to understand why incommensurate charge ordered CE type phases seem to be favoured on the hole doped side [20, 21].

An external magnetic-field applied to the CE phase also promotes canting. Experimentally, as discussed earlier, a field-induced insulator-metal transition occurs at extremely small fields. To locate the transition in our theory, we minimize and compare the energies of various 8-sublattice structures *in a field*, including the JT-*distorted* canted CE state, the *undistorted* canted state with the optimal (high) canting angle, etc. We find that for $g/t < 5$ the ground state switches in a first-order transition from a distorted canted CE phase (with the canting hardly changing the JT distortions) to an undistorted highly-canted (or FM) phase with increasing field. At the transition, the system becomes metallic, there is a jump in the magnetization (Fig. 4), and an abrupt

relaxation of all the JT distortions to zero. The transition fields have very little to do with the magnetic energy scales, but are determined by the JT energies and depend strongly on g/t as is clear from Fig. 4. For $g/t \gtrsim 6.8$, the ferromagnetic state is insulating and no insulator-metal transition can be found, which puts a bound on the values of g/t that are appropriate. In the range $5.0 \lesssim g/t \lesssim 6.8$, which may be relevant for manganites (we need $g/t \gtrsim 5.0$ to explain the existence of the A-CO phase [4] [see Fig. 1]), we find an instability of the distorted canted CE phase towards creation of defects, which suggests that the field-induced metallic phase in this case has the above mentioned two types of electrons. In all cases, there are abrupt changes in JT distortions at the transition, converting it from second-order (for progressive canting) to first-order, in agreement with recent experiments [17, 18].

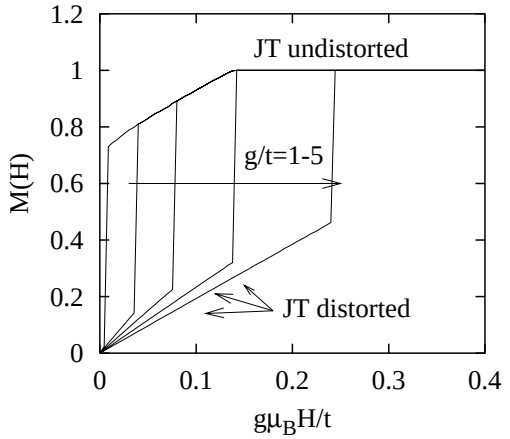

FIG. 4: Magnetization vs. field ($g/t = 1{-}5$, $J_{AF}S^2/t = 0.15$). The first-order transitions to an *undistorted* highly canted (or fully FM) metallic phase is accompanied with a relaxation of the JT distortions.

However, the transition fields obtained in our calculations are too large compared to experiments. For instance, $g\mu_B H_c \sim 0.1t$ (Fig. 4), gives $H_c \sim 140$ T (with $t \sim 0.2$ eV). The discrepancy is connected with the overestimation of the charge gap in our model. Three effects need to be included to obtain a more realistic, reduced estimate for the charge gap. First, the finiteness of the Hund's coupling, here taken to be infinite, which would allow for hopping even between sites with anti-aligned core spins; second, the cooperative nature of the JT phonons, causing sizeable distortions on the corner sites of the CE phase as well; and third, small second neighbour hopping. All of these would contribute to reducing the gap. Indeed, if we use the experimentally observed charge gap in place of the charge gap obtained in our model and then estimate the transition field, we get numbers in good agreement with observations.

In conclusion, we have provided new theoretical insights into the physics of half-doped manganites. We suggest the existence of and competition between canting (i.e., not full ferromagnetism, which could be checked by neutron diffraction) induced metallicity and inhomogeneity arising from the trapping of carriers by JT defects. It explains several features of the doping-induced (e.g. the particle-hole asymmetry) and field-induced insulator-metal transition. These ideas suggest a new two-fluid model with localized and mobile electrons, which extends the work of ref. 15 to include orbital and charge order, which when treated with more sophisticated methods such as DMFT can yield a satisfactory and complete theory of doped manganites including the regime near half-doping.

O.C. would like to thank G. Bouzerar, T. Chatterji, G. Jackeli, D. Khomskii, Y. Motome, H. Nojiri and T. Ziman for stimulating discussions. OC and HRK acknowledge financial support from IFCPAR, grant 2404-1.

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